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## 14. ABSTRACT

The dynamic behavior of laminar flames was studied for a wide range of conditions. The parameters considered included the fuel type, reactant composition, flame temperature, and combustion mode. The derived experimental data constitute a basis for partially validating the combustion chemistry for fuels ranging from hydrogen to gaseous and liquid hydrocarbons and alcohols. Emphasis was given to kinetics regimes that have not been systematically probed and/or in which current knowledge of combustion chemistry appears to be inadequate. The phenomena of ignition, propagation, and extinction were studied experimentally in the counterflow configuration. The experiments were modeled through the use of a quasi one-dimensional code and included detailed description of chemical kinetics and molecular transport. The results of this research showed that state of the art kinetics models have notable limitations in predicting flame properties even for simple molecules such as H<sub>2</sub> and C<sub>1</sub>-C<sub>2</sub> hydrocarbons, with these limitations being more profound for the more complex liquid hydrocarbons. It was also found that for H<sub>2</sub> flames, uncertainties in diffusion coefficient calculations could have a greater effect on the predicted flame properties compared to kinetics.

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# EXPERIMENTAL AND DETAILED NUMERICAL STUDIES OF FUNDAMENTAL FLAME PROPERTIES OF GASEOUS AND LIQUID FUELS

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## Executive Summary

The main goal of this research was to provide fundamental data on the dynamic behavior of laminar flames for a wide range of conditions. The parameters considered included the fuel type, reactant composition, flame temperature, and combustion mode. The derived experimental data constitute a basis for partially validating the combustion chemistry of a large number of fuels ranging from hydrogen to gaseous and liquid hydrocarbons and alcohols. Emphasis was given to kinetics regimes that have not been probed systematically in past flame studies and/or in which current knowledge of combustion chemistry appears to be inadequate. The understanding of the oxidation kinetics of such fuels is of immediate interest to the design of advanced air-breathing propulsion devices. The experiments were performed in the counterflow configuration, and the flow velocities were determined through the use of Digital Particle Image Velocimetry. Laminar flame speeds and extinction strain rates were determined, as they are both fundamental flame properties and sensitive to chemical kinetics. Additionally, ignition states in both premixed and non-premixed configurations were determined for a wide range of fuels. The experiments were modeled through the use of a quasi one-dimensional code and included detailed descriptions of chemical kinetics, molecular transport, and thermal radiation. The results of this research convincingly showed that current state of the art kinetics models have notable limitations in predicting flame properties even for simple molecules such as  $H_2$  and  $C_1$ - $C_2$  hydrocarbons, with these limitations being more profound for the more complex liquid hydrocarbons. It also was found that for  $H_2$  flames, uncertainties in diffusion coefficient calculations could have a greater effect on the predicted flame properties compared to kinetics, a result that further complicates current approaches aiming towards kinetics validation.

This research was performed by the PI, two Research Associates (Dr. Yufei Dong and Dr. Gurhan Andac), and two graduate students (Jeff Langille and Adam Holley). The following journal papers were authored:

1. "Measurement of Laminar Flame Speeds through Digital Particle Image Velocimetry: Mixtures of Methane and Ethane with Hydrogen, Oxygen, Nitrogen, and Helium," by Y. Dong, C. M. Vagelopoulos, G. Spedding, and F. N. Egolfopoulos, *Proceedings of the Combustion Institute* **29**: 1419-1426 (2002).
2. "Non-Premixed Ignition of  $H_2$  and CO by Vitiated Air in Counterflow Configurations," by J.A. Langille, Y. Dong, M.G. Andac, F.N. Egolfopoulos, and T.T. Tsotsis submitted for consideration at the 30<sup>th</sup> Symposium (International) on Combustion.
3. "Premixed Flame Extinction of Practical Liquid Fuels: Experiments and Simulations," by A.T. Holley, A. Balteria, Y. Dong, Y. Fan, M.G. Andac, and F.N. Egolfopoulos, submitted for consideration at the 30<sup>th</sup> Symposium (International) on Combustion.

4. "Premixed Extinction of  $H_2$ /Air Flames: Chemical Kinetics and Diffusion Effects," by Y. Dong, A.T. Holley, M.G. Andac, F.N. Egolfopoulos, S.G. Davis, P. Middha, and H. Wang, submitted for consideration at the 30<sup>th</sup> Symposium (International) on Combustion.
5. "An Optimized Kinetic Model of  $H_2$ /CO Combustion," by S.G. Davis, A.V. Joshi, H. Wang, and F.N. Egolfopoulos, submitted for consideration at the 30<sup>th</sup> Symposium (International) on Combustion.

## Technical Summary

### 1.0 Introduction

The accurate knowledge of the oxidation kinetics of hydrocarbon fuels is essential for the design of the next generation of air-breathing engines operating at speeds and altitudes that are noticeably greater compared to the ones currently achieved. State-of-the-art knowledge of hydrocarbon oxidation chemistry is limited to that of  $H_2$  and  $CH_4$ . For example, the GRI-3.0 mechanism [1] closely predicts a wide range of flame properties for  $H_2$  and  $CH_4$  mixtures with air, especially at high temperatures. However, even  $H_2$  and  $CH_4$  oxidation kinetics at low temperatures have not been probed systematically in previous flame studies. The oxidation kinetics of higher carbon hydrocarbons are subjected to significant uncertainties even at the  $C_2$ -level [e.g., 2]. Furthermore, systematic flame studies of liquid hydrocarbons are limited compared to the gaseous ones.

This research was both experimental and numerical. The experimental measurements focused on the determination of global flame properties of relevance to the phenomena of ignition, propagation, and extinction, and a number of innovations were introduced. For example, while propagation and extinction typically are treated as high-temperature phenomena for hydrocarbons, subsets of their kinetics also were probed at low temperatures. This probing was achieved by studying ultra-lean and/or highly diluted hydrogen flames. Such flames can be sustained at temperatures as low as 900 K, a regime of interest for hydrocarbon ignition. Additionally, the high-temperature kinetics were validated against flame extinction data obtained for a wide range of fuels, such as CO,  $C_1$ - $C_3$  hydrocarbons, and liquid fuels ( $C_7$ - $C_8$  hydrocarbons and alcohols). While laminar flame speeds cannot always be determined directly, extinction strain rates (in counterflow configurations) can, and a methodology has been introduced to do so. It has been shown that similar kinetics pathways control propagation and extinction [2]. An alternative technique also was introduced for studying flame ignition in counterflow configurations by using vitiated air that is produced from the oxidation of ultra-lean  $H_2$ /air flames as the ignition source, rather heated air. The ignition behavior of several fuels thus was tested. The final innovation included constant flame temperature experiments for a given fuel and pressure and variable fuel concentration. These conditions could be achieved by controlling the ratio of  $O_2$  to  $N_2$  in the oxidizer. Thus, any kinetics deficiencies of sufficiently off-stoichiometric mixtures would not be masked behind the uncertainties associated with small values of measured properties. Such is the case when the flame temperature is also reduced with stoichiometry.

## 2.0 Experimental and Numerical Methodologies

The experiments were performed in the opposed-jet configuration and through the use of a recently developed correlation image velocimetry (CIV) technique [3], a variation of the digital particle image velocimetry. Laminar flame speeds,  $S_u^o$ , were determined at the point of transition from a planar to a Bunsen flame as had been proposed by Vagelopoulos and Egolfopoulos [4] (VE98). The use of CIV allowed the determination of the instantaneous velocity field just before the transition initiates. Thus, the instantaneous strain rate,  $K$ , and the attendant  $S_u^o$  could be measured *directly*. The extinction strain rate,  $K_{ext}$ , also was measured *directly* by establishing flames very close to extinction and by reducing (for fuel-lean conditions) the fuel flow rate [5,6] rather than increasing the strain rate; the latter procedure also requires extrapolations. The experiments were modeled by using a quasi one-dimensional code and detailed description of molecular transport, chemical kinetics, and thermal radiation [7]. The chemical kinetics schemes tested included (1) the GRI30 mechanism [1] for  $C_1$ - $C_3$  hydrocarbons, (2) the  $H_2/O_2$  mechanism of Mueller et al. [8], (3) a mechanism developed by Wang and coworkers [9] for  $C_1$ - $C_6$  hydrocarbons, (4) three mechanisms for methanol and ethanol oxidation [10-12], and (5) two mechanisms describing  $C_7$ - $C_8$  hydrocarbon oxidation [13,14].

## 3.0 Results and Discussion

### 3.1 Propagation and Extinction of $C_1$ - $C_3$ Hydrocarbon/Air Premixed Flames

Figure 1 compares the measured  $S_u^o$ 's and those determined in VE98 with laser Doppler velocimetry (LDV) for  $CH_4$ /air mixtures at various equivalence ratios ( $\phi$ 's). Ref. 3 contains the pertinent methodology and results described in this section. The two sets of data are in close agreement, which is an independent validation of the accuracy of the CIV-derived data. The numerically determined  $S_u^o$ 's also are shown in Fig. 1, and close agreement can be seen in general. The inset depicts the dependence of the predicted  $S_u^o$  on the number of grid points used in the simulations. There is a systematic over-prediction of the experimental  $S_u^o$ 's as the mixture becomes progressively leaner.

The discrepancies between experimental and predicted  $S_u^o$  for very lean mixtures have not attracted proper attention, as the observed differences of 1-2 cm/s typically are considered to lie within experimental uncertainties. This difference occurs because as  $\phi$  decreases,  $S_u^o$  decreases as a result of the flame temperature reduction. Thus, if  $S_u^o$  is to be used for validating chemical kinetics for a wide range of  $\phi$ 's, the proper way to do it is by keeping the flame temperature constant as  $\phi$  changes so that concentration effects are isolated from those of temperature [15].

Figure 2 depicts experimental and predicted  $S_u^o$ 's for  $CH_4/O_2/N_2$  mixtures as functions of  $\phi$ , keeping the adiabatic flame temperature,  $T_{ad}$ , constant by modifying the relative  $O_2/N_2$  free-stream concentrations;  $T_{ad}$  was determined by equilibrium calculations. For all three  $T_{ad}$ 's investigated i.e. 1900, 2000, and 2100 K,  $S_u^o$  exhibits a non-monotonic behavior. For  $\phi < 1$  mixtures,  $S_u^o$  increases as  $\phi$  decreases. Species consumption and sensitivity analyses showed that as  $\phi$  decreases the rate of the main branching reaction  $H + O_2 \rightarrow OH + O$  (R1) is enhanced as the  $O_2$  concentration increases for the same  $T_{ad}$ . For  $\phi > 1$  mixtures,  $S_u^o$  first increases and then decreases as  $\phi$  increases.  $S_u^o$  increases because the  $O_2$  concentration increases relative to  $N_2$  in order to maintain the same  $T_{ad}$ . Thus, the rate of R1 is enhanced. Subsequently, the mixture reactivity is reduced as the  $CH_4$  concentration increases to the point that it effectively scavenges

H radicals through the reaction  $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$  (R2) competing for H radicals with R1, whose rate is reduced. As a result the burning rate is also reduced.

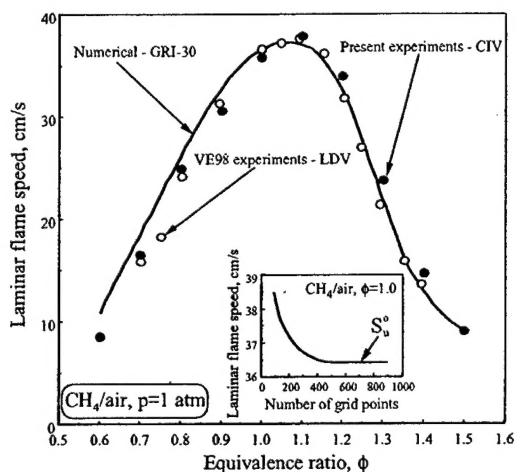


Fig. 1. Comparisons between the experimentally measured  $S_u^o$  data for atmospheric  $\text{CH}_4/\text{air}$  mixtures with those of VE98 and predictions using the GRI30 mechanism.

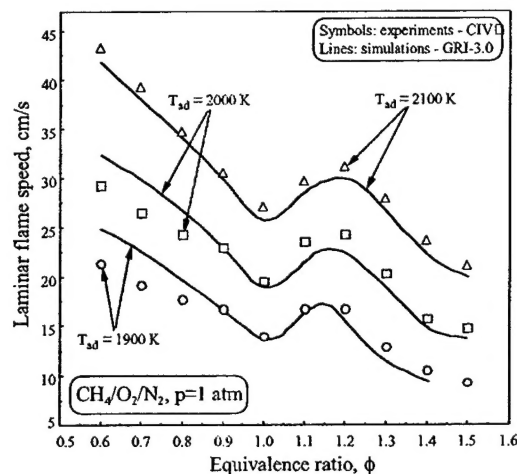


Fig. 2. Variation of experimental and predicted  $S_u^o$  with  $\phi$  and flame temperature for atmospheric  $\text{CH}_4/\text{O}_2/\text{N}_2$  mixtures.

Comparing the experimental and predicted  $S_u^o$ 's, there is a close agreement for near-stoichiometric and rich flames. While for lean flames the agreement is very close for  $T_{ad} = 2100$  K, for the lower  $T_{ad}$ 's the experiments were notably over-predicted by the simulations. The observed discrepancies are greater than the experimental uncertainty, which had been determined to be less than 3%.

Extinction data were derived for fuel-lean mixtures of air with  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_3\text{H}_8$ , and  $\text{C}_3\text{H}_6$  by utilizing the single flame configuration that results by counterflowing mixtures against an air jet. Given that it was possible to measure the  $K_{ext}$  values *directly*, focus was on using  $K_{ext}$ 's for model validation. Because, there is always a small but finite uncertainty associated with the determination of  $S_u^o$ 's, either as a result of the presence of residual stretch or the need of using fitting formulas to extract  $S_u^o$ . Figures 3 through 8 depict experimental and numerical  $K_{ext}$ 's for single, lean premixed  $\text{CH}_4/\text{air}$ ,  $\text{C}_2\text{H}_6/\text{air}$ ,  $\text{C}_2\text{H}_4/\text{air}$ ,  $\text{C}_2\text{H}_2/\text{air}$ ,  $\text{C}_3\text{H}_8/\text{air}$ , and  $\text{C}_3\text{H}_6/\text{air}$  flames. The inability of the GRI30 mechanism [1] to predict  $K_{ext}$ 's other than  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  flames is apparent and in agreement with a previous study [2]. The Wang mechanism [9] was tested against the  $\text{C}_2\text{H}_2/\text{air}$ ,  $\text{C}_3\text{H}_8/\text{air}$ , and  $\text{C}_3\text{H}_6/\text{air}$  data. Although the simulations under-predicted somehow the experiments, the agreement is, in general, fairly good.

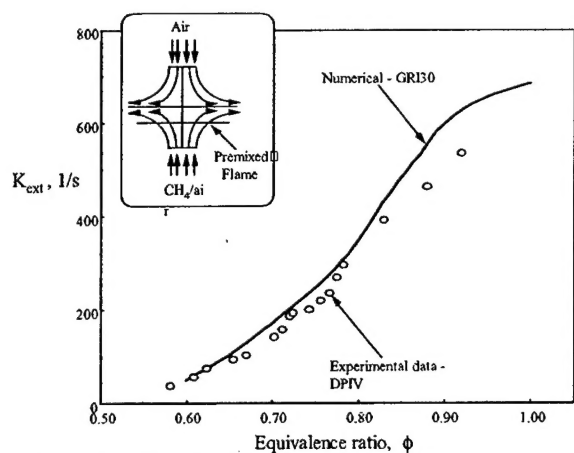


Fig. 3.  $K_{ext}$  for single  $\text{CH}_4/\text{air}$  flames

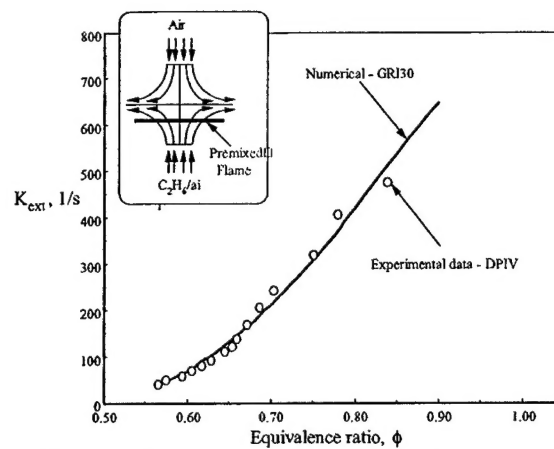


Fig. 4.  $K_{ext}$  for single  $\text{C}_2\text{H}_6/\text{air}$  flames

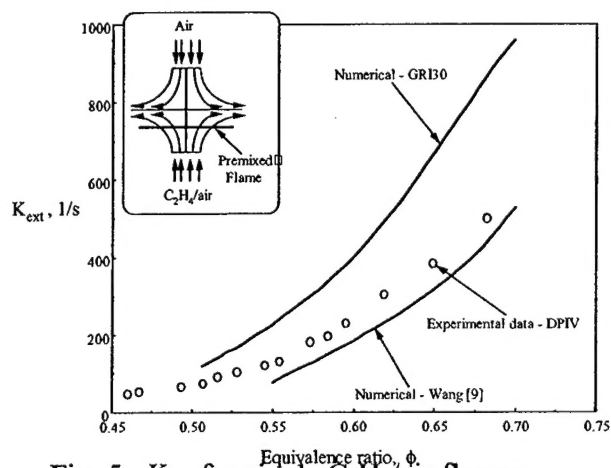


Fig. 5.  $K_{ext}$  for single  $\text{C}_2\text{H}_4/\text{air}$  flames

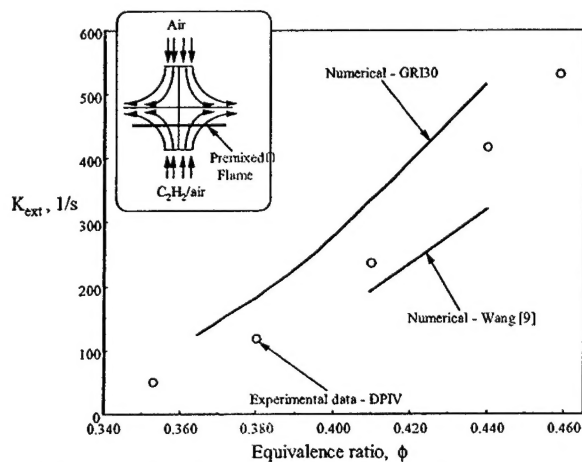


Fig. 6.  $K_{ext}$  for single  $\text{C}_2\text{H}_2/\text{air}$  flames

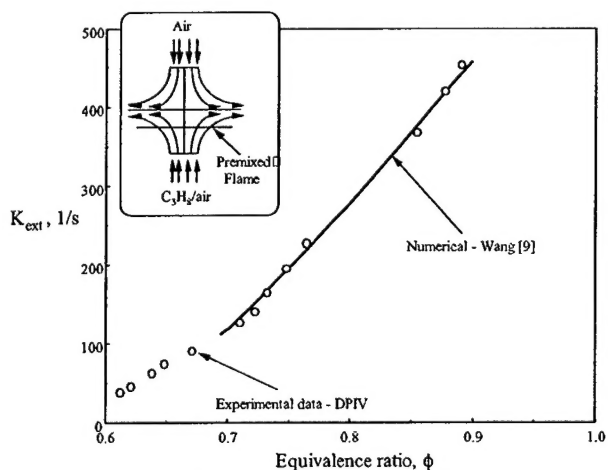


Fig. 7.  $K_{ext}$  for single  $\text{C}_3\text{H}_8/\text{air}$  flames

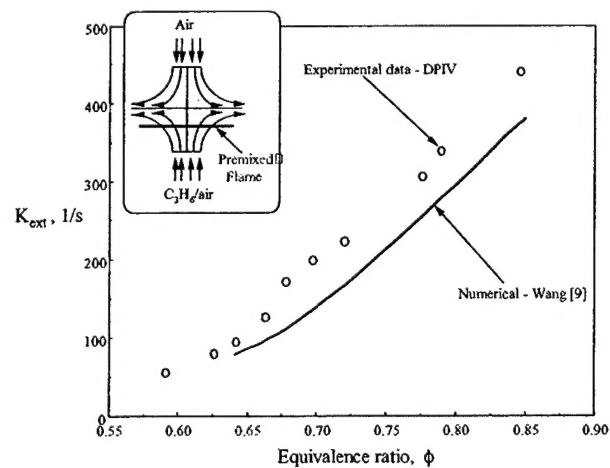


Fig. 8.  $K_{ext}$  for single  $\text{C}_3\text{H}_6/\text{air}$  flames



### 3.2 Premixed Flame Extinction of Mixtures of Liquid Fuels with Air

The extinction of mixtures of practical liquid fuels with air also was studied in the single flame configuration; Ref. 5 contains the pertinent methodology and results described in this section. The introduction of the liquid phase into the air under room temperature was achieved through the use of an evaporator and a high-precision liquid pump. The liquid was atomized into a stream of heated air, and subsequently the temperature of the mixture was reduced to ambient. The liquid fuel existed in the vapor phase as long as its partial pressure was maintained below its vapor pressure at the prevailing ambient temperature. The liquid fuels that were tested were  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $n\text{-C}_7\text{H}_{16}$ , and  $\text{iso-C}_8\text{H}_{18}$ . The  $K_{ext}$ 's of mixtures of those fuels with air at ambient temperature are shown in Fig. 9.

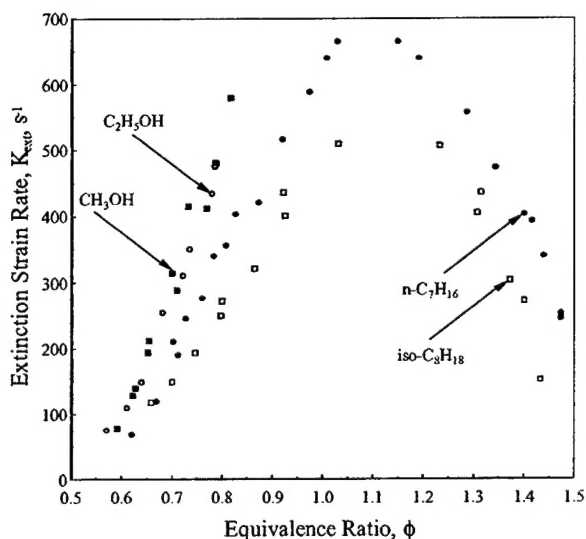


Fig. 9.  $K_{ext}$  for mixtures of air with liquid fuels

The  $K_{ext}$ 's of the alcohol fuels are notably higher than those of  $n\text{-C}_7\text{H}_{16}$ , and  $\text{iso-C}_8\text{H}_{18}$ , while there are minor differences between the measured  $K_{ext}$ 's of  $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$  flames. Furthermore, the  $n\text{-C}_7\text{H}_{16}$  flames are more resistant to extinction than  $\text{iso-C}_8\text{H}_{18}$  flames. These observations are important in terms of combustion stability.

Figure 10 depicts the  $K_{ext}$  and  $S_u^o$  values for methanol/air mixtures at various  $\phi$ 's;  $S_u^o$ 's were taken from Ref. 16. The  $K_{ext}$  data are slightly under-predicted by the Held and Dryer [10] mechanism (HD98) for  $\phi < 0.75$  and the agreement is much closer for  $\phi > 0.75$ . Comparing the  $S_u^o$ 's reveals that the HD98 mechanism over-predicts the data for the entire range of  $\phi$ 's. The Fischer et al. [11] mechanism (FDC00) satisfactorily predicts the  $S_u^o$ 's for lean  $\phi$ 's; it under-predicts the  $K_{ext}$ 's in the same  $\phi$ -range by a factor of nearly 3. Figure 11 depicts  $K_{ext}$  and  $S_u^o$  values for ethanol/air mixtures at various  $\phi$ 's.  $S_u^o$ 's were taken from Ref. 17. Both the FDC00 and the Marinov [12] (MRN99) mechanisms under-predict the experimental  $K_{ext}$  by nearly a factor of 2. The  $S_u^o$ 's are slightly over-predicted over the entire range of  $\phi$  by FDC00. The MRN99 mechanism slightly over-predicts  $S_u^o$ 's on the lean side and slightly under-predicts them for near-stoichiometric and rich flames.

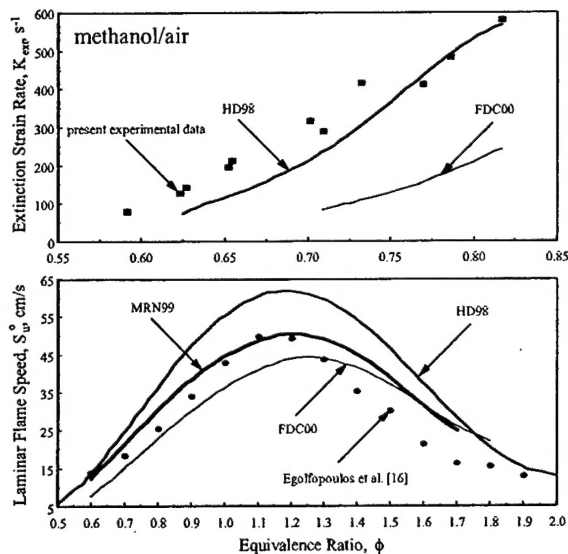


Fig. 10.  $K_{ext}$  and  $S_u^o$  for methanol/air.

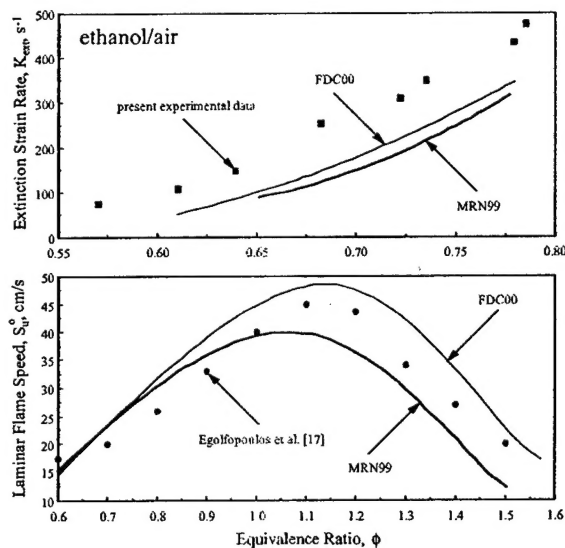
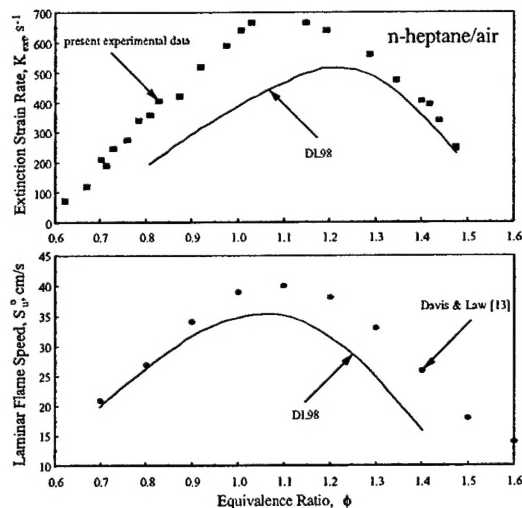
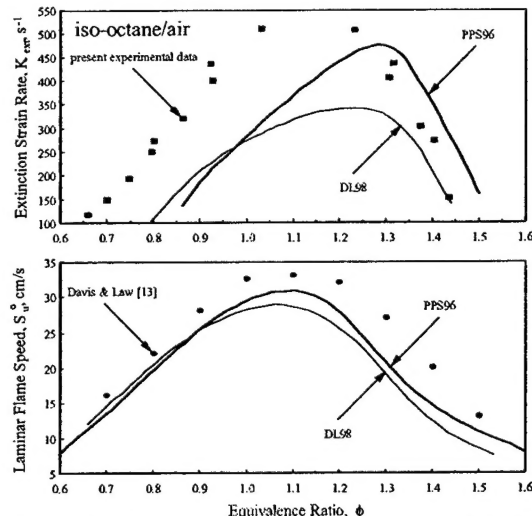


Fig. 11.  $K_{ext}$  and  $S_u^o$  for ethanol/air.

Figure 12 depicts the  $K_{ext}$  and  $S_u^o$  values for n-heptane/air mixtures at various  $\phi$ 's. The experiments were modeled using the Davis & Law [13] mechanism (DL98). While  $S_u^o$ 's are closely predicted on the fuel-lean side and under-predicted on the fuel-rich side, the opposite is true for  $K_{ext}$ . More specifically, on the fuel-lean side the experimental  $K_{ext}$ 's are under-predicted by nearly a factor of 2, while on the fuel-rich side a close agreement is observed. The predicted  $K_{ext}$  peaks at about  $\phi = 1.22$ , while the experimental  $K_{ext}$  at about  $\phi = 1.08$ .

Figure 13 depicts the  $K_{ext}$  and  $S_u^o$  values for iso-octane/air mixtures at various  $\phi$ 's. The experiments were modeled using both the DL98 and Pitsch et al. [14] (PPS96) mechanisms. It is apparent that both mechanisms fail to predict the experimental  $K_{ext}$ 's, especially on the fuel-lean side where the experimental data are under-predicted by factors of 2 to 3. Furthermore, the experimental  $K_{ext}$  peaks around  $\phi = 1.15$ , while the DL98 predicts the peak approximately around  $\phi = 1.25$ , and PPS96 predicts the peak around  $\phi = 1.30$ . On the fuel-rich side PPS96 over-predicts the experimental  $K_{ext}$ 's, while DL98 under-predicts them. The observed disagreements on the fuel-rich side are less than the ones observed on the fuel-lean side. Both mechanisms result in rather similar  $S_u^o$  values for the entire  $\phi$ -domain. They both predict closely the experimental  $S_u^o$ 's for fuel-lean mixtures, while they under-predict them on the fuel-rich side.



Fig. 12.  $K_{ext}$  and  $S_u^o$  for n-heptane/air flamesFig. 13.  $K_{ext}$  and  $S_u^o$  for iso-octane/air flames

Comparisons between experimental data and numerical predictions revealed that for the liquid fuels studied in this investigation, kinetics mechanisms that closely predict laminar flame speeds fail to predict the attendant extinction strain rates. However, this inconsistency was not found to be the case for mixtures of air with methane, a fuel whose oxidation kinetics are well characterized. The observed discrepancies could be attributed to the fact that the validation of kinetics mechanisms of the liquid fuels is not as comprehensive as that for methane. As a result, the ability of such mechanisms to predict flame phenomena even at relatively similar conditions, such as propagation and extinction, may be compromised. This finding is of interest for large-scale simulations of practical combustors.

### 3.3 Chemical Kinetics and Diffusion Effects in Premixed Extinction of $H_2$ /air Flames

The oxidation kinetics of  $H_2$  were tested under fuel-lean conditions for which the presence of thermo-diffusional instabilities does not allow for the determination of laminar flame speeds; Refs. 6 and 18 contain the pertinent methodology and results described in this section. Under such conditions the flame temperatures are well below those encountered in hydrocarbon flames. Such temperatures are relevant to the process of ignition. The extinction strain rates,  $K_{ext}$ , were determined and used to validate the kinetics, as it is known that both extinction and propagation are controlled by similar chain mechanisms [2]. The presence of positive stretch suppresses the formation of cellular structures. Figure 14 depicts comparisons between the experimental and predicted  $K_{ext}$ 's using the GRI30 [1] and Mueller et al. [8] ("MKYD99")  $H_2/O_2$  mechanisms. Both experiments and simulations were performed in the single-flame configuration in which a mixture jet counterflows against an ambient temperature air-jet. The agreements are not close, and there is a difference in the "slope" of the results. While the predicted  $K_{ext}$ 's by the two mechanisms "merge" at high temperatures, they deviate significantly from each other at lower temperatures. The GRI30 mechanism appears to under-predict the  $K_{ext}$ 's of ultra-lean  $H_2$ /air flames by a factor of two (!) at low temperatures. At high temperatures, both mechanisms appear to over-predict the experimental  $K_{ext}$ 's by nearly 50%. The numerical simulations that are shown in Fig. 14 were performed by using a large number of grid points,  $N$ . It was found that, by varying  $N$  from 300 to 2000-3000,  $K_{ext}$  could increase by as much as 25%, reaching asymptotically the values that are reported in Fig. 14 as  $N \rightarrow \infty$ .

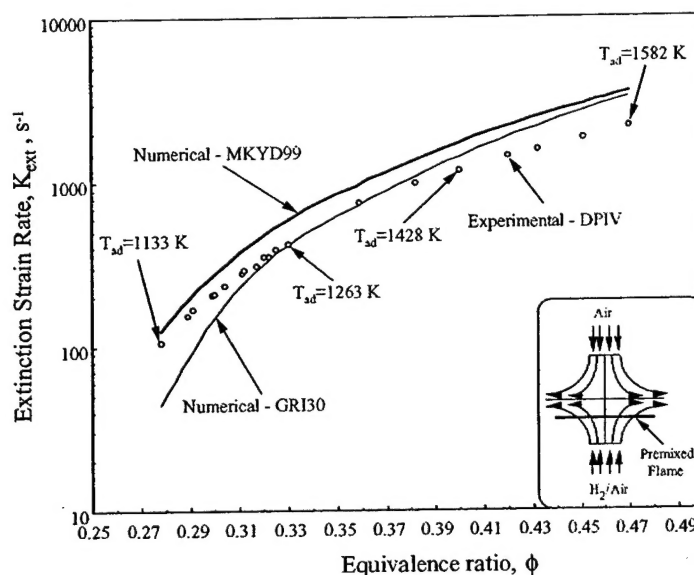


Fig. 14.  $K_{ext}$  for single  $H_2$ /air flames

Through detailed sensitivity analysis, it was also shown that the extinction states of such mixtures are not only sensitive to the kinetics but also to the species diffusivities. Thus, validation of models against flame data of such highly diffusive mixtures must be done by considering the uncertainties associated with both kinetics and diffusion.

In view of this consideration, an additional contribution of this study was the advancement of an improved treatment of the mass diffusion coefficients [6]. Figure 17 depicts comparisons between the experimental and predicted  $K_{ext}$ 's for these models (GRI30, "MKYD99", and a trial model "TRM04" and an optimized model "OPM04" [19]). The simulations shown in both Figs. 15a and 15b included the use of the updated multi-component diffusion model. Significant disagreements exist between experimental and predicted  $K_{ext}$ 's, and there is a difference in the "slope" of the results. Detailed simulations also showed that the predicted extinction strain rates based on the updated formulation of diffusion coefficients were different by ~15-25% from those obtained using the Sandia transport coefficient compilation (Fig. 16). Similarly, it was found that by using mixture-averaged versus full multi-component formulation could affect the predicted extinction strain rates by as much as 25-40%. From a kinetics point of view differences of the order of 15-40% in predicting global flame properties are rather large and could have a major impact on rate constants.

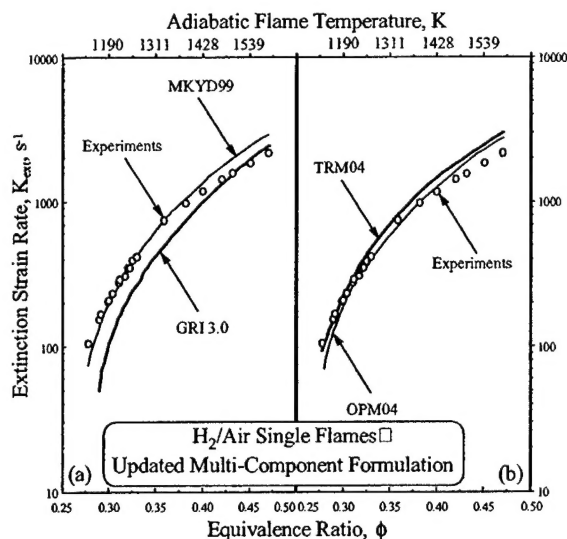


Fig. 15. Experimental and numerical  $K_{ext}$  for single ultra-lean  $H_2$ /air flames. The effect of reaction model is shown.

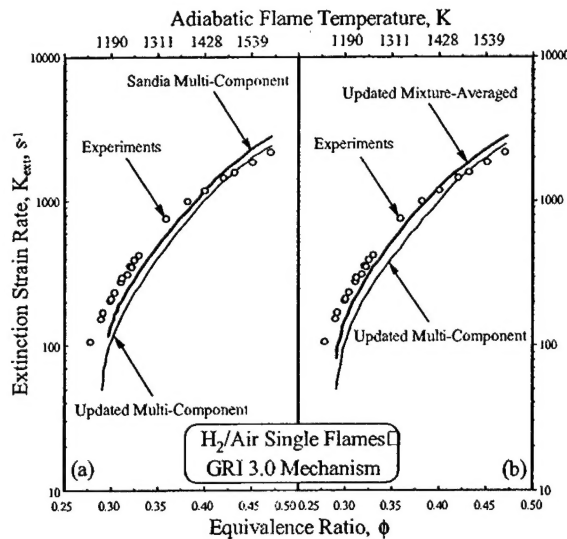


Fig. 16 Experimental and numerical  $K_{ext}$  for single ultra-lean  $H_2$ /air flames. The effect of diffusion model is shown.

In order to moderate the diffusion effects additional experiments were performed, by determining  $K_{ext}$ 's for  $N_2$ -diluted near-stoichiometric  $H_2$ /air mixtures. The results are shown in Figs. 17 and 18 for  $\phi = 0.777$  and  $0.965$ , respectively. In these studies the associated  $T_{ad}$ 's vary from 1600-1700 K down to  $\sim 1200$  K, thus accessing similar flame temperatures as those of ultra-lean flames. The numerical simulations were conducted using the updated multi-component diffusion model and all four kinetic models. The results reported for both  $\phi = 0.777$  and  $0.965$  exhibit very similar behavior to those of Fig. 15, in which the updated multi-component diffusion also was used. For low  $T_{ad}$ 's (high  $N_2$ -dilution) GRI30 under-predicts the experimental data by a factor of  $\sim 2$  and over-predicts them at high  $T_{ad}$ 's. For both  $\phi$ 's MKYD99 predicts closely the low- $T_{ad}$  data and over-predicts the high- $T_{ad}$  data by a factor of 1.5-2. The predictions of TRM04 and OPM04 are consistent with those of Fig. 15 at the corresponding  $T_{ad}$ 's.

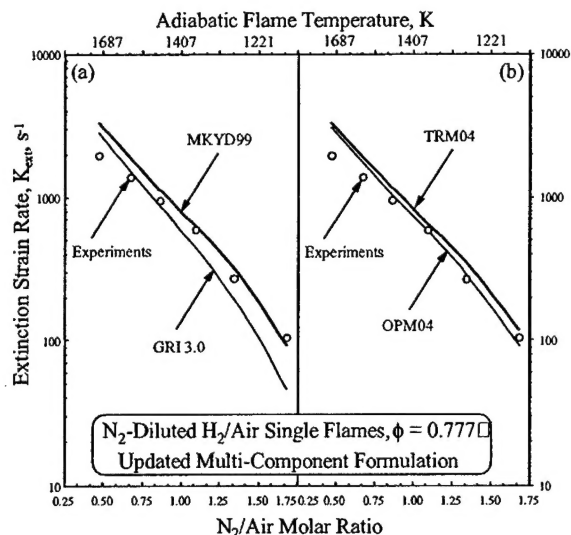


Fig. 17. Experimental and numerical  $K_{ext}$  for  $N_2$ -diluted,  $\phi = 0.777$   $H_2$ /air flames. The effect of reaction model is shown.

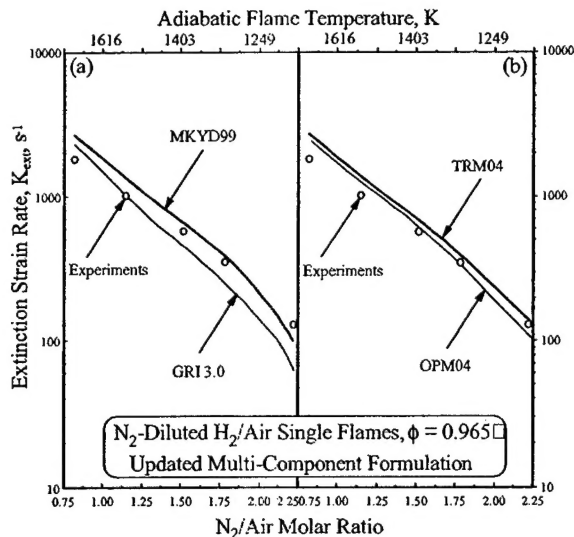


Fig. 18. Experimental and numerical  $K_{ext}$  for  $N_2$ -diluted,  $\phi = 0.965$   $H_2$ /air flames. The effect of reaction model is shown.

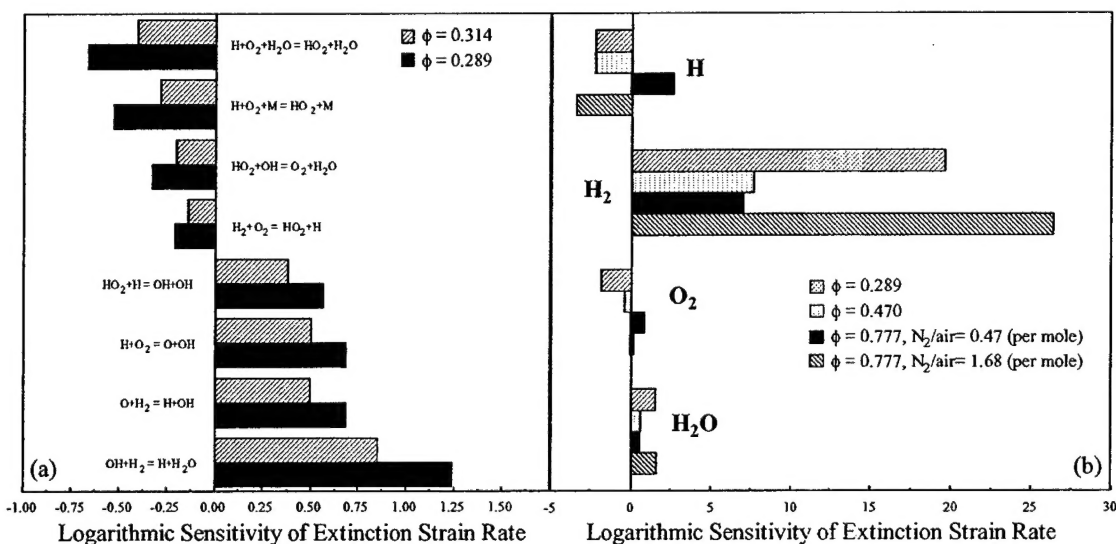


Fig. 19. Logarithmic sensitivity coefficients of reactions and mass diffusion coefficients on  $K_{ext}$  for ultra-lean and  $N_2$ -diluted near-stoichiometric  $H_2$ /air flames calculated using the TRM04 model.

Figure 19 depicts the logarithmic sensitivity coefficients of  $K_{ext}$  on the kinetics and mass diffusion coefficients for ultra-lean  $H_2$ /air flames with  $\phi = 0.289$  and  $\phi = 0.314$ . While the logarithmic sensitivity coefficients for kinetics are at most around the value of one (Fig. 19a), the corresponding ones for diffusion (Fig. 19b) well exceed one, and, in particular, for the  $H_2$  values of the order of 10 to nearly 30(!) are realized.

### 3.4 Non-Premixed Ignition of $H_2$ and Gaseous Hydrocarbons

A new approach was developed for ignition studies in the counterflow configuration. It includes the use of ultra-lean  $H_2$ /air flames as the ignition source; Ref. 19 contains the pertinent methodology and results described in this section. The hot excess air dominates the composition of the post-flame products, while minor amounts of  $H_2O$  are present. The temperature of those products can be controlled by either varying the  $H_2$ /air equivalence ratio or by adding small amounts of CO in cases in which higher ignition temperatures and low strain rates are required. Alternatively, in cases in which ignition temperatures below 1100 K were required a platinum screen was used at the burner exit to catalytically support  $H_2$ /air flames at such low temperatures. The temperature just downstream of the platinum screen was measured by a thermocouple and was used as boundary condition in the numerical simulations. The use of the platinum screen was required for the ignition of  $H_2$ ,  $C_2H_4$ , and  $C_2H_2$  while the use of  $H_2$ /air flames at various equivalence ratios and with various amounts of added CO is required for the ignition of saturated hydrocarbons. Premixed ignition was achieved by counter-flowing the hot products against an air-jet in which the fuel was slowly added to the air stream. Non-premixed ignition was achieved by counter-flowing the hot products against a  $N_2$  jet in which the fuel was slowly added. The non-premixed ignition of  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ , and  $C_3H_8$  has been studied. Figure 20 depicts the effect of  $H_2$  and  $C_2H_4$  addition on the ignition of  $CH_4$  for a global strain rate,  $K_g = 44 \text{ s}^{-1}$ . These data were determined by using a  $\phi = 0.30$   $H_2$ /air flame as the ignition source, and by adding various amounts of  $H_2$  and  $CH_4$  in various mixtures of  $C_2H_4/N_2$ . These results are of relevance to the ignition response of the products of thermal cracking of endothermic fuels [e.g. 2]. The ignition promotion caused by  $H_2$  and  $C_2H_4$  is apparent. Numerical studies showed that no mechanism could predict the experimental results shown in Fig. 20.

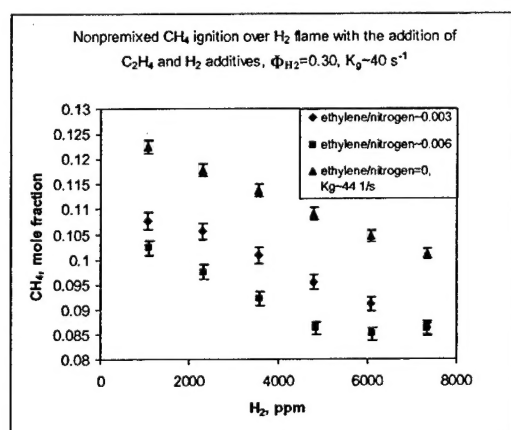


Fig. 20. Non-premixed ignition of gaseous fuels

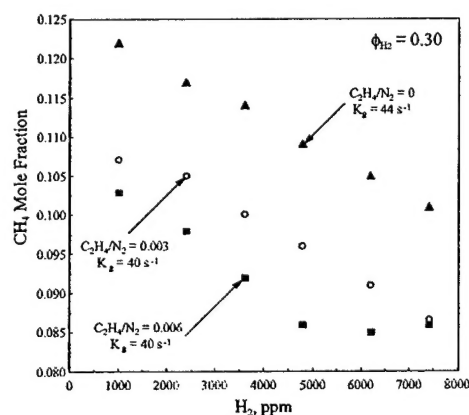


Fig. 21. Premixed ignition of liquid fuels

### 3.5 Premixed Ignition of Liquid $\text{CH}_3\text{OH}$ , $\text{C}_2\text{H}_5\text{OH}$ , $n\text{-C}_7\text{H}_{16}$ , and $\text{iso-C}_8\text{H}_{18}$ Fuels

The premixed ignition of practical liquid fuels has been also studied. Representative results are shown in Fig. 21 and have been achieved by increasing the temperature of a  $\phi=0.256$   $\text{H}_2$ /air flame through CO addition. As expected, the higher was the temperature of the  $\text{H}_2$ /CO/air flame the lower was the ignition equivalence ratio of the test fuel. The greater ignition propensity of the alcohol fuels as well as that of  $\text{iso-C}_8\text{H}_{18}$  compared to  $n\text{-C}_7\text{H}_{16}$  is notable.

### REFERENCES

1. G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, S. Song, W.C. Gardiner, Jr., V. Lissianski & Z. Qin, GRI-Mech 3.0, [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/) (2000).
2. Egolfopoulos, F.N. & Dimotakis, P.E., *Combust. Sci. Tech.* **162**, pp. 19-36, (2001).
3. Dong, Y., Vagelopoulos, C.M., Spedding, G.R. & Egolfopoulos, F.N. *Proc. Combust. Inst.* **29**: 1419-1426 (2002).
4. Vagelopoulos, C.M. & Egolfopoulos, F.N. *Proc. Combust. Inst.* **27**: 513-519 (1998).
5. Holley, A.T., Balteria, A., Dong, Y., Fan, Y., Andac, M.G. & Egolfopoulos, F.N. "Premixed Flame Extinction of Practical Liquid Fuels: Experiments and Simulations," submitted for consideration at the 30<sup>th</sup> *Symposium (International) on Combustion*.
6. Dong, Y., Holley, A.T., Andac, M.G., Egolfopoulos, F.N., Davis, S.G., Middha, P. & Wang, H. "Premixed Extinction of  $\text{H}_2$ /Air Flames: Chemical Kinetics and Diffusion Effects," submitted for consideration at the 30<sup>th</sup> *Symposium (International) on Combustion*.
7. Egolfopoulos, F.N. & Campbell, C.S., *J. Fluid Mech.* **318**, pp 1-29 (1996).
8. Mueller, M.A., Kim, T.J., Yetter, R.A. & Dryer, F.L., *Int. J. Chem. Kin.* **31**, pp 113-119 (1999).
9. Wang, H., Personal Communications (2003).
10. T.I. Held & F.L. Dryer, *Int. J. Chem. Kin.* **30(11)**, pp. 805-830 (1998).
11. S.L. Fischer, F.L. Dryer & H.J. Curran, *Int. J. Chem. Kin.* **32(12)**, pp. 713-740 (2000).
12. N.M. Marinov, *Int. J. Chem. Kin.* **31(3)**, pp. 183-220 (1999).
13. Davis, S.G. & Law, C.K., *Proc. Combust. Inst.* **27**: 521-527 (1998).
14. H. Pitsch, N. Peters & K. Seshadri, *Proc. Combust. Inst.* **26**: 763-771 (1996).
15. Zhu, D.L., Egolfopoulos, F.N. & Law, C.K. *Proc. Combust. Inst.* **22**: 1537-1545 (1988).
16. Egolfopoulos, F.N., Du, D.X. & Law, C.K. *Combust. Sci. Tech.* **83** (1992) 33-75.
17. Egolfopoulos, F.N., Du, D.X. & Law, C.K. *Law Proc. Combust. Inst.* **24** (1992) 833-841.
18. Davis, S.G., Joshi, A.V., Wang, H. & Egolfopoulos, F.N. "An Optimized Kinetic Model of  $\text{H}_2$ /CO Combustion," submitted for consideration at the 30<sup>th</sup> *Symposium (International) on Combustion*.
19. Langille, J.A., Dong, Y., Andac, M.G., Egolfopoulos, F.N. & Tsotsis, T.T. "Non-Premixed Ignition of  $\text{H}_2$  and CO by Vitiated Air in Counterflow Configurations," submitted for consideration at the 30<sup>th</sup> *Symposium (International) on Combustion*.